One-step Synthesis of Ag₃PO₄/Ag Photocatalyst with Visible-light Photocatalytic Activity

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A highly efficient photocatalyst Ag₃PO₄/Ag was prepared by a one-step low temperature chemical bath method. The reflectance spectra (DRS) indicated Ag₃PO₄/Ag had strong absorption in visible light region. The synthesized Ag₃PO₄/Ag photocatalyst was used as the efficient photocatalysts for the photocatalytic degradation of Rhodamine B (RhB) under visible-light illumination which showed almost complete degradation (~98%) of RhB dye in 90 min. The negative surface of Ag₃PO₄/Ag photocatalyst also promoted the degradation of a cationic dye like methylene blue (MB; 78% in 90 min), while the performance against an anionic dye like methyl orange was poorer (MO; 40% in 90 min). Compared to the pure Ag₃PO₄ photocatalyst, the Ag₃PO₄/Ag photocatalyst showed the enhanced visible light photocatalytic informance. The excellent photocatalytic performance is mainly ascribed to the surface plasmon resonance of Ag nanoparticles and a large negative charge of PO₄³⁻ ions.

Keywords: Ag₃PO₄/Ag, chemical synthesis, photocatalysis, visible light

1. Introduction

Semiconductor-based photocatalysts have attracted considerable attention due to their potentially promising avenue for solving current environment and energy problems, by using the abundant solar light. Of the well-known photocatalysts, titanium oxide (TiO₂) has undoubtedly proven to be the most promising material, due to its low toxicity, earth abundance, chemical and thermal stability, and resistance to photocorrosion. Unfortunately, this commonly used photocatalyst, with a relatively wide band gap (3-3.2 eV), can only absorb a small fraction of solar energy (< 5%), which limits its practical applications. Therefore, development of more efficient photocatalysts is urgent and indispensable.

Recently, it has been demonstrated that plasmonic nanostructures of noble metals (mainly silver and gold) show significant promising in the field of photocatalysis. A series of new hybrid photocatalysts on the basis of surface plasmon resonance (SPR) of metal nanoparticles, namely, plasmonic photocatalysts, were developed to decompose various organic pollutants under visible-light irradiation. Tobaldi et al. have reported that the incorporation of Ag NPs can significantly improve the photocatalytic activity of TiO₂ nanopowders. Chen et al. also revealed that the SPR effect of Au nanoparticles could induce visible-light-driven photocatalytic activity of Au/ZrO₂ and Au/SiO₂ photocatalyst. Ag/silver halide structure has been developed as a visible-light photocatalyst to enhance the photocatalytic activity of semiconductor, such as Ag/AgCl, Ag/AgBr, and Ag/AgI. These catalysts displayed high photocatalytic activity and good stability under visible light due to the localized surface plasmon resonance (LSPR) effect of silver nanoparticles produced on the surface of silver halide.

Silver orthophosphate (Ag₃PO₄), a new type of photocatalyst reported by Ye et al., has been demonstrated to show excellent photocatalytic ability for O₂ evolution from water as well as great photodecomposition of organic compounds. Interestingly, in order to promote the charge separation efficiency of the Ag₃PO₄ semiconductor, selective growth of Ag₃PO₄ submicron-cubes on Ag nanowires to construct necklace-like hetero-photocatalysts and two-dimensional dendritic Ag₃PO₄ nanostructures was demonstrated by this group. The effect of particle size, pH value, and morphology of silver phosphate on its photocatalytic activity have also been investigated. Unfortunately, one major limitation of this novel photocatalyst is the instability upon photo-illumination, since it is easily corroded by the photogenerated electrons (4Ag₃PO₄ + 6H₂O + 12h+ + 12e− → 12Ag + 4H₃PO₄ + 3O₂). Therefore, it is highly desirable to develop effective strategies to improve the stability of the Ag₃PO₄ photocatalyst. Recent reports indicated that AgX (X=Cl, Br, I) nanoshells on the surface of Ag₃PO₄ can enhance their photocatalytic properties and stability. Furthermore, carbon quantum dots, graphene oxide, TiO₂, Bi₂MoO₆, SnO₂, and Fe₂O₃ were successfully used to form Ag₃PO₄ based hybrid nanostructures for getting enhanced photocatalytic activity and stability. The origin of photocatalytic performance of Ag₃PO₄ using first-principles density functional theory was investigated. The excellent photocatalytic performance of Ag₃PO₄ is partly attributed to the highly dispersive band structure of the conduction-band minimum (CBM) resulting from Ag s–Ag s hybridization without localized d states.
Inspired by this study, Ag/Ag₃PO₄ was successfully synthesized as highly efficient and stable plasmonic photocatalyst. However, most of the reported synthesis methods require surfactant, such as using pyridine, or in relatively complicated process. Here, we design a one-pot, simple experimental approach to prepare the Ag₃PO₄/Ag photocatalyst to improve the stability of Ag₃PO₄. The photocatalytic activity evaluation was carried out by decomposing methyl orange (MO), rhodamine (RhB) and methyl blue (MB) under visible irradiation at room temperature. Based on the experimental results, the photocatalytic reaction mechanism of the Ag₃PO₄/Ag plasmonic photocatalyst was discussed.

2. Experimental

2.1. Preparation of Ag₃PO₄/Ag photocatalyst

All the reagents used in this work were in analytical grade without further purification, and purchased from Shanghai Reagents Company (Shanghai, China). Bare Ag₃PO₄ powder samples were prepared by the simple ion-exchange method. In a typical synthesis, 0.018 mol AgNO₃ was dissolved in 100 mL of DI water. Na₂HPO₄ aqueous solution (0.12 M) was added drop by drop to the solution, under magnetic stirring, until the initial white colour changed to yellow. The resulting products were washed with DI water for several times, and finally dried at 70 °C for 5 h in a vacuum.

The Ag₃PO₄/Ag plasmonic photocatalysts were prepared by a one-step low temperature chemical bath method. In a typical synthetic route, 0.005 mol of silver nitrate (AgNO₃) was added to 50 ml ethylene glycol (EG) under vigorous stirring, and the resultant solution was marked as solution A. The solution which was marked as solution B results from the dissolution of Na₂HPO₄·12H₂O (0.001 mol) in 50 ml EG under vigorous stirring. When solutions A and B became clear, they were mixed together and stirred for 2 h until to assure homogeneity. The solution was heated in an oil bath at 160 °C for 30 min. The resulting precipitates were washed with DI and absolute ethanol several times and then dried at 70 °C for 5 h. A schematic diagram of the catalyst preparation process is shown in Figure 1.

2.2. Characterization of photocatalysts

The X-ray powder diffraction (XRD) patterns of the as-prepared catalysts were characterized by using a Bruker D8 advance powder X-ray diffractometer with Cu Kα radiation (λ=1.54056 Å) in the 2θ range from 20° to 70°. Field-emission scanning electron microscope (FESEM, JEOL-6300F) was employed to characterize the morphologies and size of the synthesized samples. UV-vis diffuse reflectance spectra were obtained for the dry pressed disk samples by using a Shimadzu UV 2550 recording spectrophotometer, which was equipped with an integrating sphere, and BaSO₄ was used as a reference.

A Zeta potential analyzer, (Zetapals, Brookhaven Instruments Corporation, USA) was used to characterize the electrokinetic properties of the Ag₃PO₄/Ag photocatalysts. For the Zeta potential measurement, an Ag₃PO₄/Ag photocatalyst suspension of 2 mg/ml concentration was prepared by dispersing Ag₃PO₄/Ag powder in deionized water under continuous magnetic stirring. The effect of pH (in the range of 5-11) on the electrokinetic properties was investigated by measuring the zeta potential under distinct pH values, changed by using 0.1 M HNO₃ (in the acidic range) and 0.1 M (alkaline range) solutions.

2.3. Evaluation of photocatalytic performance

MO (anionic dye), MB and RhB (cationic dyes) were selected as model chemicals to evaluate the activity and properties of the Ag₃PO₄/Ag photocatalyst. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) equipped with an ultraviolet cutoff filter to provide visible light was used as the light source. The distance between it and the photocatalyst was 50 cm. The light intensity reaching the samples was measured using a radiometer and was found to be approximately 35 W m⁻² in the visible-light range. In a typical experiment, 250 ml aqueous suspensions of

![Figure 1. A schematic diagram of the preparation process of Ag₃PO₄/Ag photocatalyst.](image-url)
RhB (10 mg/L) and 100 mg of photocatalyst powders were placed in a test tube. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under room air equilibrated conditions. At given irradiation time intervals, about 5 ml of the suspension was collected and centrifuged to remove the catalyst particulates for analysis. The residual dye absorption property was detected using a UV-vis spectrophotometer (Hitachi UV-3100).

3. Results and Discussions

The crystalline structure of the as-prepared sample has been examined, as shown in Figure 2. Figure 2a shows the typical powder X-ray diffraction (XRD) pattern of the product. It can be clearly seen that the diffraction peaks can be indexed to the pure body-centered cubic (bcc) structure of Ag\(_2\)PO\(_4\) with cell constant of \(a=6.013\) Å (JCPDS no. 84-512). Figure 2b is a typical XRD pattern of the as-obtained Ag\(_2\)PO\(_4\)/Ag sample. All the diffraction peaks in this pattern can be categorized into two sets. The diffraction peaks that marked with “▼” can be readily indexed to cubic Ag\(_2\)PO\(_4\) (JCPDS no. 84-512), while the peak labeled with “★” can be indexed to cubic phase Ag (JCPDS no. 87-717). No other crystalline impurities can be observed. The strong diffraction peaks of Ag indicate the good crystallinity degree of Ag in the Ag\(_2\)PO\(_4\)/Ag plasmonic photocatalyst.

The morphology and size of the pure Ag\(_2\)PO\(_4\) and the Ag\(_2\)PO\(_4\)/Ag were investigated with SEM and TEM techniques. Figure 3a depicts a typical SEM micrograph of the pure Ag\(_2\)PO\(_4\) sample, revealing the spherical morphology with uniform size of about 800-900 nm. Figure 3b shows a SEM image of the prepared Ag\(_2\)PO\(_4\)/Ag photocatalyst. It can be seen that Ag\(_2\)PO\(_4\)/Ag photocatalyst is composed of many tiny spherical Ag\(_2\)PO\(_4\) nanoparticles dispersed on the surface of the spherical Ag particles. Figure 3c shows the representative TEM micrographs of Ag\(_2\)PO\(_4\)/Ag photocatalyst. As shown in Figure 3c, the TEM image confirms that a large quantity of Ag\(_2\)PO\(_4\) nanocrystals are attached onto the surface of the spherical Ag, and the size of Ag\(_2\)PO\(_4\) nanoparticles is mostly in the range of 100-200 nm.

The UV-Vis diffuse reflectance spectra of as-prepared Ag\(_2\)PO\(_4\) and Ag\(_2\)PO\(_4\)/Ag photocatalysts are shown in Figure 4. It is observed that pure Ag\(_2\)PO\(_4\) could absorb visible light with a wavelength shorter than 530 nm (shown in Figure 4a), in agreement with the results previously reported\(^{15}\). However, for Ag\(_2\)PO\(_4\)/Ag plasmonic photocatalyst, except for a much higher absorbance than Ag\(_2\)PO\(_4\), at the range of 500-800 nm, a new broad absorbance peak at 320 nm has been observed, which should be ascribed to the metallic Ag particles (shown in Figure 4b). Remarkable absorption enhancement in visible light region is beneficial for improving photocatalytic activity in this irradiation region.

The photocatalytic performances of Ag\(_2\)PO\(_4\)/Ag plasmonic photocatalyst and of pure Ag\(_2\)PO\(_4\) particles for the RhB degradation have been studied and are compared in Figure 5. As shown in this figure, it can be clearly seen that the Ag/Ag\(_2\)PO\(_4\) composite shows a higher photocatalytic activity for the decomposition of RhB compared with Ag\(_2\)PO\(_4\) photocatalyst. Furthermore, the photocatalytic stability of Ag\(_2\)PO\(_4\)/Ag was investigated by recycling in the repeated RhB degradation experiments. As shown in Figure 6, the RhB dye is quickly bleached after every RhB decomposition experiments, and Ag\(_2\)PO\(_4\)/Ag photocatalysts are stable enough during the repeated experiments without exhibiting any significant loss of photocatalytic activity. Therefore, the as-prepared Ag\(_2\)PO\(_4\)/Ag composites can work as effective photocatalysts for organic compounds degradation with good...
stability in the absence of electron acceptors. To elucidate the photocatalytic reaction mechanism, the main species including h\(^+\), •O\(_2^-\) and •OH involved in the photocatalytic process was examined. The method was applied according to the Xiang’s report without any modifications\(^1\). The results indicated that h\(^+\) and •O\(_2^-\) were the main reactive oxidizing species in photocatalytic reaction process of Ag\(_3\)PO\(_4\)/Ag composites.

Furthermore, to demonstrate the photocatalytic activities of the synthesized Ag\(_3\)PO\(_4\)/Ag plasmonic photocatalyst for the degradation of distinct organic pollutants, we conducted photocatalytic degradation experiments of RhB, MB and MO. Figure 7a shows the adsorption spectrum of RhB dye over the prepared Ag\(_3\)PO\(_4\)/Ag photocatalyst. As seen from the observed UV-vis, the absorption peak characteristic of this dye (554 nm) decreases gradually with the increasing of the illumination time. After 90 min irradiation, RhB color was destained by about 98%. The adsorption spectrum of MB in aqueous solution under the same condition is shown in Figure 7b. It indicates that the concentration of MB is decreased as the irradiation time increasing by measuring the intensity of characteristic absorption peak (665 nm), and MB is degraded 78% after 90 min. Finally, discoloration of MO in aqueous solution was tested, by measuring the attenuation of adsorption peak (465 nm) intensity over irradiation time. Again, the color attenuation was observed (Figure 7c), but in a less overall extent (about 40% after 90 min of irradiation) than registered with the previous dyes. Differences in discoloration efficiencies for RhB, MB, and MO dyes can be compared in Figure 7d. The photocatalyst now prepared shows much better performance against cationic dyes (RhB and MB) than to discoloring the anionic dye (MO) solution.

Attempting to clarify that difference, zeta potential measurements for a series of aqueous Ag\(_3\)PO\(_4\)/Ag suspensions of variable pH values were performed, as shown in Figure 8. The negative values of zeta potential reveal that the as-obtained particles show negative surface charge. Thus, the cationic dye molecules (RhB or MB) could be easily absorbed onto the catalyst surface by electrostatic attraction forces, and charge transfer is facilitated. By contrast, anionic dye molecules (MO) tend to be repulsed and as consequence the action of Ag\(_3\)PO\(_4\)/Ag plasmonic photocatalyst is less effective.

Based on these results, a possible mechanism is proposed to explain that the enhanced photocatalytic activity and stability of the Ag\(_3\)PO\(_4\)/Ag plasmonic photocatalyst is due to the synergistic effects between the Ag\(_3\)PO\(_4\) nanoparticles and the Ag nanoparticles, as shown in Figure 9. First, the deposition of Ag\(_3\)PO\(_4\) nanoparticles on the surface of the Ag nanoparticles can effectively protect Ag\(_3\)PO\(_4\) from dissolution, since Ag nanoparticles can retain/store electrons. The photogenerated electrons can be transferred to Ag\(_0\) nanoparticles instead of remaining in Ag\(_3\)PO\(_4\) lattice. This will inhibits the reduction of Ag\(_3\)PO\(_4\), and then will reduce the molecular oxygen to form the O\(_2^-\) active species. Second, The LSPR produced by the collective oscillations of surface electrons on Ag nanoparticles could enhance the local inner electromagnetic field. The electrons generated by the Ag\(_3\)PO\(_4\) could be separated efficiency with the help of the local electromagnetic field. Finally, PO\(_4^{3-}\) ions own large negative charge and will attract positive holes while repelling
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... electrons. Then, photogenerated holes tend to remain on the surface of Ag₃PO₄ nanoparticles. Meanwhile, PO₄³⁻ ions have strong bonding affinity for H₂O molecules. As is well known, H₂O molecules could be easily adsorbed on the surface and then be oxidized by the holes to OH⁻ radicals, being these active apecies to oxidize the dye molecule into carbon dioxide molecules. The above aspects together contributed to the enhanced photocatalytic activity and improved stability of the Ag₃PO₄/Ag plasmonic photocatalyst compared to pure Ag₃PO₄ particles.

4. Conclusions

This work developed a facile approach for the synthesis of Ag₃PO₄/Ag plasmonic photocatalyst. The novel material shows poorer performance in discoloring anionic dye solutions, such as MO dye, in comparison to cationic dyes (RhB and MB). This behavior can be well explained in terms of the exposed negative surface of the Ag₃PO₄/Ag photocatalyst. High efficiency of Ag₃PO₄/Ag photocatalyst arises from LSPR of silver nanoparticles and large negative charge of PO₄³⁻ ions. It is a promising candidate for the removal of hazardous organic materials from wastewater.

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References


